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ScienceDirect
Polyhedron 25 (2006) 3330–3336
POLYHEDRON
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Studies on cobalt(II) complexes with *N*-thioacylamido(thio)phosphates: X-ray crystal structure of the Co[PhC(S)NP(S)(OPr*i*)$_2$]$_2$

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Received 17 January 2006; accepted 7 June 2006
Available online 13 June 2006

Abstract

Reaction of the potassium salts of *N*-thioacylamidophosphates RC(S)NHP(O)(OPr*i*)$_2$ (R = Ph, PhNH, *p*-MeOPhNH, *p*-BrPhNH, *i*PrNH, *t*BuNH, Et$_2$N, *c*-C$_5$H$_{10}$N, *c*-OC$_4$H$_8$N, *c*-C$_5$H$_{11}$NH) with Co(II) cation in aqueous EtOH leads to the complexes of Co(L-O,S)$_2$ type structure. Complexes Co(B)L$_2$ were obtained by the reaction of chelate complexes CoL$_2$ (R = Ph, PhNH) with 2,2′-bipyridine and 1,10-phenanthroline. Structures of the compounds obtained were investigated by EIMS, IR, UV–Vis spectroscopy and microanalysis. Complex Co[PhC(S)NP(S)(OPr*i*)]$_2$ was investigated by single crystal X-ray diffraction.

Keywords: Organoelement analogues of β-dicarbonyl ligands; *N*-Thioacylamido(thio)phosphates; Cobalt(II) chelates; Crystal structure; UV–Vis spectra

1. Introduction

N-(Thio)acylamido(thio)phosphates RC(X)NHP(Y)R′$_2$ (X, Y = O or S; R = Alk, Ar, ArNH, AlkNH, Alk$_2$N; R′ = OAlk, OAr, Ar) are important because of the variety of ways of interaction with d^8- and d^{10}-metal cations [1]. These compounds and their complexes can be used as extractants, analytical reagents [2] and structural fragments for construction of metal-containing macrocycles [3] and polycrown-compounds [4].

Dithioderivatives of these compounds, *N*-thioacylamidothiophosphates RC(S)NHP(S)R′$_2$ (**1**) [5–8] or their diphosphorus analogues R$_2$P(X)NHP(X)R′$_2$ (X = S, Se) [9,10] and their complexes with divalent d-metal cations have been extensively investigated. Formation of chelate complexes of the ML$_2$ structure is characteristic for them. Ligands are coordinated bidentately in these compounds, through the atoms of sulfur of the thiocarbonic and thio(seleno)phosphoric groups. Cobalt(II) chelates with oxygen-containing ligands RC(O)NHP(O)R′$_2$ (**2**) show the expressed propensity to oligomerization in the solid phase and to the formation of complexes with the solvent molecules. Dimeric structures of complexes have been studied, e.g. complexes Co$_2$[L]$_4$D$_2$, where [L] = [CCl$_3$C(O)NP(O)(OMe)$_2$]$^-$ or [CCl$_3$C(O)NP(O)(NHBz)$_2$]$^-$; D = *i*PrOH [11,12]. An attempt to synthesise the heteroligand Co(II) complexes by reaction of Co(PPh$_3$)$_2$Cl$_2$ or Co(PPh$_3$)$_2$NO$_2$ with Ph$_2$P(Se)NHP(Se)Ph$_2$ was unsuccessful [13]. Only the [Co(Ph$_2$P(Se)NHP(Se)Ph$_2$)$_2$] complex was obtained.

The structure of the Co(II) cation coordination compounds with RC(S)NHP(O)R′$_2$ (**3**) (HL) ligands, containing donor atoms of sulfur and oxygen simultaneously is practically not studied. On the one hand, prevalence of

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0277-5387/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2006.06.005